Supplementary Materials (S)

Pilot Study on Human Exposure to Microplastics in Intraocular Fluids and Bisphenols in Serum: Analytical Detection and Characterisation

Supplementary Materials Part A – sampling methods and method development platform A (the reduced Methods & Materials section)

Table S1. Clinical characteristics of patients

Patient number	Sample type	Age/Population	Disease	Gender	Ophthalmic surgery history	Implants hystory (type, material)
1	AH1, BS1	74 / Elder	Cataract (OD)	Female	Not operated previously	No implants in the body
2	AH2, BS2	84 / Elder	Cataract (OS)	Female	Previously operated (11/2024) (OD)	Implanted intraocular lens Tecnis PCB 00
3	AH3, BS3, VH1	78 / Elder	Combined cataract and epiretinal membrane (OD)	Male	Not operated previously	No implants in the body
4	AH4, BS4	67 / Elder	Cataract surgery (OS)	Male	Previously operated (11/2024) (OD)	Intraocular lens implanted (type unknown)
5	AH5	78 / Elder	Cataract (OD)	Female	Not operated previously	No implants in the body
6	AH6	67 / Elder	Cataract (OD)	Male	Not operated previously	No implants in the body
7	AH7	62 / Adult	Cataract (OD)	Female	Not operated previously	No implants in the body
8	AH8	80 / Elder	Cataract (OS)	Female	Previously operated (02/2025) (OD)	Implanted intraocular lens Bausch and Lomb MX60 intraocular lens; no other implants
9	AH9	80 / Elder	Cataract (OS) .	Male	Previously operated (Surgery date unknown) (OD)	Intraocular lens implanted (type unknown). no other implants
10	BS5 VH2	18 / Adult	Pars plana vitrectomy and retinotomy OS, silicone oil removal OS	Male	Previously operated (02/2025), with silicone oil (5000 mPas) instilled into the vitreous space;	No other implants
11	AH10	80 / Elder	Cataract (OS)	Male	Previously operated- retinal ablation (02/2025) (OD) with silicone oil (5000 mPas) instilled into the vitreous space;	Implanted intraocular lens and silicone oil 10 years ago (unknown data for lens and silicone oil)

Patient number	Sample type	Age/Population	Disease	Gender	Ophthalmic surgery history	Implants hystory (type, material)
12	AH11 BS6 VH3	53 / Adult	Pars plana vitrectomy and removal of silicone (OD)	Male	Previously operated (09/2024) (OD), with silicone oil instilled into the vitreous space	Implanted intraocular lenses (OU) (implanted years ago,unknown data for lens and silicone oil): No other implants
13	AH12 BS7	70 / Elder	Cataract (OS)	Female	Previously operated (10/2024) (OD)	Implanted intraocular lenses (OD) (TECNIS PCB00)
14	AH13 BS8	78 / Elder	Cataract (OD)	Male	Previously operated (02/2025) (OS)	Implanted intraocular lenses (OS) (TECNIS PCB00)
15	AH14 BS9	85/ Elder	Cataract (OS)	Male	Previously operated (02/2025) (OD)	Implanted intraocular lenses (OS) (TECNIS PCB00)
16	AH15 BS10	70 / Elder	Cataract (OD)	Male	Not operated previously	No implants in the body
17	AH16 BS11	72 / Elder	Cataract (OS)	Female	Not operated prevously	No implants in the body
18	AH17 BS12	66 / Elder	Cataract (OD)	Male	Not operated previously	No implants in the body
19	AH18	71 / Elder	Cataract (OD)	Male	Not operated previously	No implants in the body
20	AH19 BS13	63 / Adult	Anterior vitrectomy and anterior chamber irrigation (OD)	Male	Previously operated (06/2024) (OD)	Implanted experimental artificial lens capsule (VaMa, material: medical silicone = polydimethylsiloxane) and simultaneously implanted artificial intraocular lens (Tecnis ZCB 00)

OD, oculus dextrus; OS, oculus sinister; OU, oculus utruisque

Supplementary Methods A-S1. Surgical-environment sampling and airborne deposition calculation

Pre-combusted 400-mL glass beakers were deployed at eye level (1–1.8 m) for alternating 12-h intervals (working vs. non-working hours) over three days (n=12), following Field et al. [1]. After collection, beakers were rinsed with pre-filtered distilled water and filtered through glass-fibre filters (25 mm diameter, 1.2 μm pore size, Whatman GF/C™). Filters were dried and prepared for MP examination. MP flux (μg m^{-2} day^{-1}) was calculated by multiplying the MP mass per filter by 227.27, the conversion factor from the bottom area of the 400-mL beaker to m^2, and by 2 to convert the 12-h collection to a daily value.

Supplementary Methods A-S2. Ocular-fluid method development, digestion and filtration

Method development used AH and VH from five female Simmental cows older than 2.5 years. After thawing, samples were homogenised using a Vortex 3 (IKA-Werke GmbH & Co. KG, Staufen, Germany), transferred with glass Pasteur pipettes into pre-cleaned Safe-Lock tubes (Eppendorf AG, Hamburg, Germany), and centrifuged at 14,800 rpm for 10 min. Approximately 100 mg of sample was weighed using an AND BM-5 semi-microbalance (A&D Company, Tokyo, Japan). Organic matrix digestion used 1 mL of 30% H_2O_2 (Gramm-mol d.o.o., Zagreb, Croatia) for 12 h at 65 °C [2,3]. Digests were vacuum filtered through 25-mm, 1.2-µm Whatman GF/C™ filters pretreated at 500 °C for 8 h in an LT 40/11 muffle furnace (Nabertherm GmbH, Lilienthal, Germany). Residues were quantitatively transferred using 96% ethanol; the central 9-mm filter area was excised, placed in a glass Petri dish (Karl Hecht, Sondheim, Germany), and dried at 45 °C. Human samples followed the validated workflow with 2 mL of 30% H_2O_2 at 65 °C for 12 h and overnight filter drying at room temperature.

Supplementary Methods A-S3. Detailed Py-GC/MS and serum BP conditions

Py-GC/MS used an EGA/PY-3030D pyrolyser with AS-1020E autosampler (Frontier Lab Ltd., Fukushima, Japan) coupled to a GC-8890/MSD 5977C (Agilent, Santa Clara, CA, USA) and an Ultra Alloy-5 column (30 m × 0.25 mm × 0.50 µm; Frontier Laboratories, Saikon, Japan). EI was 70 eV; spectra were acquired at 1.56 scans/s over m/z 40–400; the interface temperature was 320 °C. Thermochemolysis used 20 µL TMAH (10% in methanol; Sigma-Aldrich, Germany). Calibration used an 11-polymer standard mixture (Frontier Laboratories Ltd., Fukushima, Japan) and 0.2 µg d5-PS/poly(4-fluorostyrene) internal standard (Polymer Source, Montreal, Canada). Validation followed EC Regulation No. 333/2007 [4] and included LOD, LOQ, specificity, linearity, repeatability/reproducibility, recovery, and matrix effects.
For serum, 490 µL was fortified with 10 µL 24BPS13C12 internal standard (500 ng/mL; Toronto Research Chemicals, Toronto, Canada) and extracted with 1.5 mL acetonitrile (Biosolve Chimie SARL, Dieuze, France), followed by 250 mg anhydrous Na_2SO_4 (Merck KGaA, Darmstadt, Germany). After centrifugation (2 min, 6000 rpm, 3864×g), supernatants were concentrated at 40 °C and 1300 rpm using an RCV2-18HCL rotational vacuum concentrator (Christ, Osterode am Harz, Germany). For derivatisation, 100 µL extract was mixed with 100 µL water, 100 µL 0.5 mol/L carbonate/bicarbonate buffer (pH 9), and 100 µL freshly prepared Dns-Cl (18 mg/mL in ACN; Merck KGaA), then incubated at 40 °C for 45 min. Excess reagent was quenched with 20 µL 250 mM NaOH for 10 min, followed by 100 µL 20% formic acid; samples were dried and reconstituted in 100 µL ACN. Separation used a 1290 Infinity UPLC (Agilent Technologies, Singapore) coupled to a G6460 ESI Triple Quad (Agilent Technologies, Waldbronn, Germany) and a Poroshell 120 EC-C18 column (100 × 2.1 mm, 2.7 µm). The column was held at 35 °C; mobile phases were 0.2% formic acid in water (A) and ACN (B) at 0.3 mL/min. The gradient was 20% B initially, 80% at 5 min, 90% at 10–11 min, and 20% at 13–16 min; injection volume was 15 µL. Positive ESI used 340 °C, 5 L/min gas flow, and 4500 V. Matrix-matched calibration covered 0.10–20 ng/mL. Validation followed EC Regulation No. 333/2007 [4].

References:

1. Field, D.T.; Green, J.L.; Bennett, R.; Jenner, L.C.; Sadofsky, L.R.; Chapman, E.; Loubani, M.; Rotchell, J.M. Microplastics in the surgical environment. *Environ. Int.* **2022**, 170, 107630.
2. Dzierżyński, E.; Gawlik, P. J.; Puźniak, D.; Flieger, W.; Jóźwik, K.; Teresiński, G.; Forma, A.; Wdowiak, P.; Baj, J.; Flieger, J. Microplastics in the Human Body: Exposure, Detection, and Risk of Carcinogenesis: A State-of-the-Art Review. *Cancers* **2024**, 16, 3703. https://doi.org/10.3390/cancers16213703

3. Barceló, D.; Picó, Y.; Alfarhan, A. H. Microplastics: Detection in human samples, cell line studies, and health impacts. *Environ. Toxicol. Phar.* **2023**, 101, 104204. https://doi.org/10.1016/j.etap.2023.104204
4. COMMISSION REGULATION (EC) No 333/2007 of 28 March 2007 laying down the methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo(a)pyrene in foodstuffs

Supplementary Materials Part B – method performance characteristics from optimisation to qualitative/quantitative calculations

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1. Pyrolysis-gas chromatography/mass spectrometry conditions

Table S2. Py-GC/MS method

EGA/PY-3030D	
Furnace	590°C (1 min)
Interface	320°C
Agilent GC 8890	
Heater	300°C
Inlet mode	Split
Split ratio	12.5 : 1
Split flow	15 mL/min
Pre-column	UA Precolumn 50-1M, film thickness 1 μm 50% diphenyldimethyl polysiloxane
Column	Ultra Alloy^{+} - MP (30 m x 0,25 mm x 0,50 μm)

	5% diphenyldimethyl polysiloxane P/N: UAMP-K01
Column flow	1.2 mL/min
Oven	40°(2 min), 4°C/min to 310°C (30 min)
MSD 5799C	
Transfer line temperature	280°C
Source	230°C
Quad	150°C
Electron energy	70eV
Acquisition type	Scan
Scan speed	1.562 (N=2)
Gain factor	1
Mass range (m/z)	40 - 400

2. Pyrolysis products monitored and MS conditions

Table S3. Main pyrolysis products of the 11 polymer cluters

Polymer	Pyrolysis products	Molecular Formula	Mw
C-PE	α-Alkenes	C_nH_{2n-2}	Series from C14 to C24 (194.36 – 366.70)
C-PP	2,4-Dimethyl-1-heptene	C_9H_{18}	126
C-PS	5-hexene-1,3,5-triyltribenzene (Styrene trimer)	$C_{24}H_{24}$	312
C-ABS	2-Phenethyl-4-phenylpent-4-enentrile	$C_{19}H_{19}N$	261
C-SBR	SB hybrid dimer	$C_{12}H_{14}$	158
C-PMMA	Methyl methacrylate	$C_5H_8O_2$	100
C-PC	Dimethyl-Bisphenol A*	$C_{17}H_{20}O_2$	256
C-PVC	Naphtalene	$C_{10}H_8$	128
C-PET	Dimethyl terephthalate*	$C_{10}H_{10}O_4$	194
C-PA6	N-Methyl-ε-caprolactam*	$C_7H_{13}NO$	127
C-PA66	Cyclopentanone	C_5H_8O	84

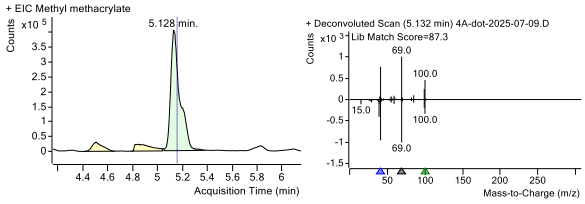
** - TMAH derivatization*

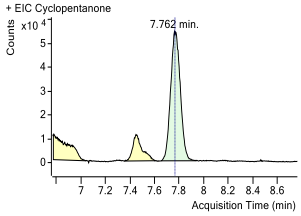
Table S4. Specific marker and ions used for quantification of the 11 polymer clusters; characteristic Py-GC/MS decomposition products used for identification and quantification of detected polymer clusters indicated by "C-" as pure polymers and potentially included polymer-related derivatives

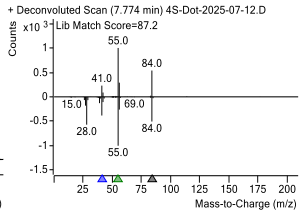
Basic polymer cluster	Cluster associated compounds	Characteristic decomposition products	Quantifier and qualifier ions m/z	Retention time
C-PMMA	PMMA; polyalkylated methacrylate, acryl-containing binder	Methyl methacrylate	41, **69**, 100	5.11
C-PA66	PA66	Cyclopentanone	41, 55, **84**	7.77
C-PP	PP, EPDM rubber	2,4-Dimethyl-1-heptene	43, **70**, 126	9.26

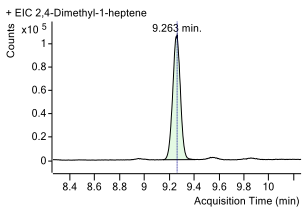
Basic polymer cluster	Cluster associated compounds	Characteristic decomposition products	Quantifier and qualifier ions m/z	Retention time
C-PVC	PVC (hard and plasticized), chlorinated rubber, chlorinated PE	Naphthalene	**128**	23.33
C-PA6	PA6	N-Methyl-εcaprolactam	44, **127**	25.25
C-SBR	SBR	SB hybrid dimer	**104**, 158	28.47
C-PE	HDPE, LDPE, PE-containing copolymers and rubbers, ethylenevinyl acetate (EVA), EPDMrubber	α,ω-Alkadienes **α-Alkenes** Alkanes	55, 69, 83, 97, 111 C14-alkene: 196 C15-alkene: 210 C16-alkene: 224 C17-alkene: 238 C18-alkene: 252 C19-alkene: 266 C20-alkene: 280 C21-alkene: 294 C22-alkene: 308 C23-alkene: 322 C24-alkene: 336	30 – 59
C-PET	PET, polybutylene terephthalate (PBT)	Dimethyl terephthalate	**163,** 194	34.1
C-PC	PC, epoxide resin	Benzene, 1,1'-(1-methylethylidene)bis[4-methoxy-	**241,** 256	49.49
C-ABS	ABS	2-phenethyl-4-phenylpent-4-enenitrile	**91**, 170	52.04
Internal standard		2,4,6-Tri(4-fluorophenyl)-hex-1-ene	**109,** 243	57.12
Internal standard	Deuterated polystyrene used as internal standard for pyrolysis	Styrene trimere d5	**96,** 121, 217	57.50
C-PS	PS, PS-containing copolymers (e.g., ABS, SAN), PS- or acryl styrene binders, varnish	5-Hexene-1,3,5-triyltribenzene (styrene trimer)	**91**, 207, 312	57.65

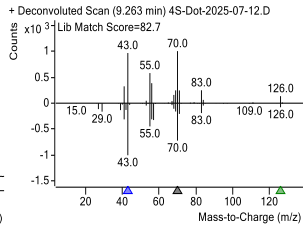
3. The chromatograms (on the left side) and mass spectrograms (on the right side) through pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) analysis of spiked AH sample, including 11 MPs polymers and 2 internal standards

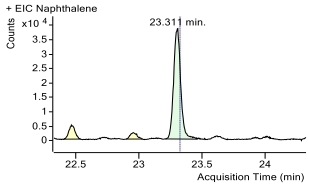


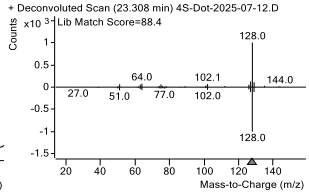

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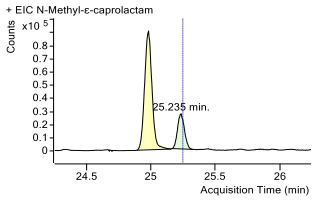

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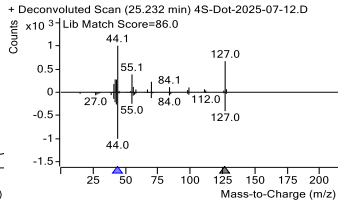

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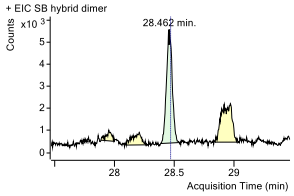

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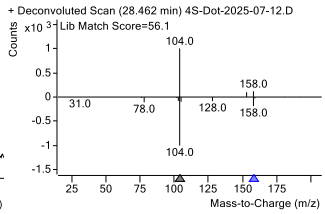

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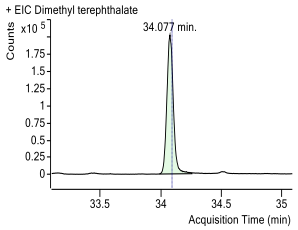

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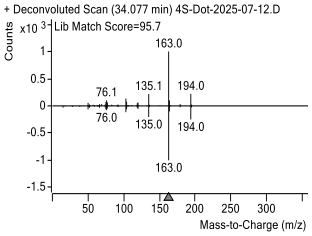

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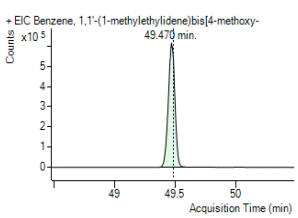

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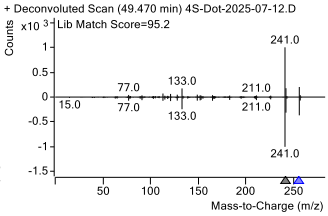

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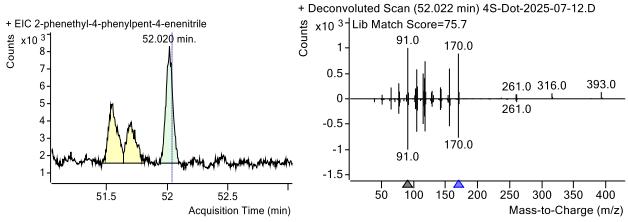

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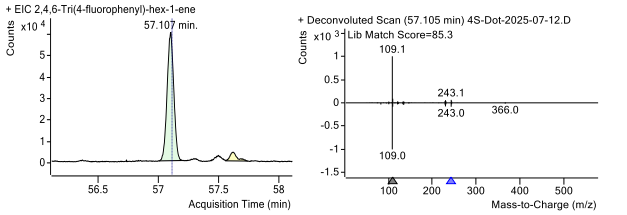

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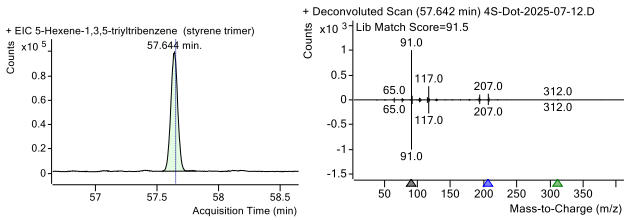

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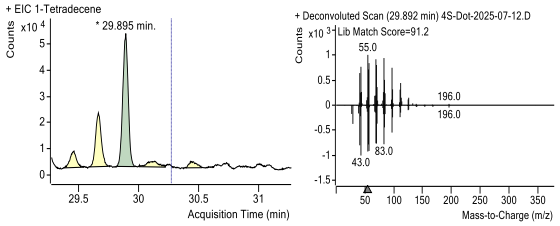

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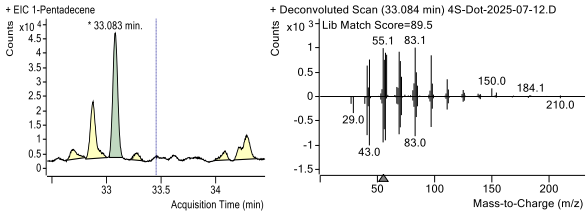

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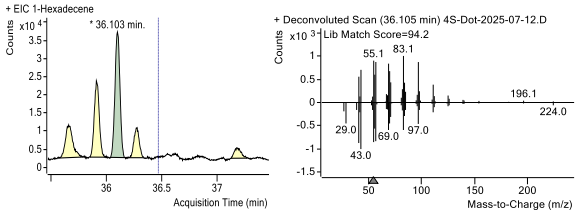

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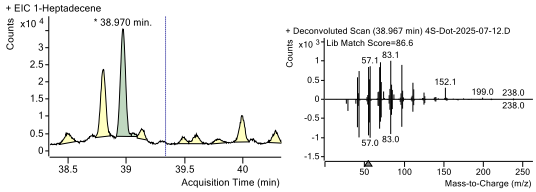

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Mass-to-Charge (m/z)

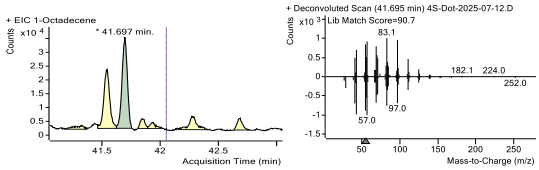

+ EIC 5-Hexene-1,3,5-triyltribenzene (styrene trimer)
57.644 min.
Counts
Acquisition Time (min)
+ Deconvoluted Scan (57.642 min) 4S-Dot-2025-07-12.D
Lib Match Score=91.5
91.0
117.0
65.0
207.0
312.0
Mass-to-Charge (m/z)

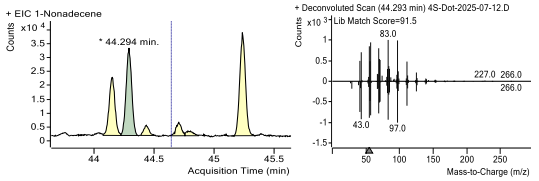

+ EIC 1-Tetradecene
* 29.895 min.
Counts
Acquisition Time (min)
+ Deconvoluted Scan (29.892 min) 4S-Dot-2025-07-12.D
Lib Match Score=91.2
55.0
196.0
83.0
43.0
Mass-to-Charge (m/z)

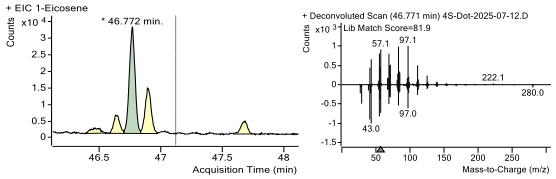

+ EIC 1-Pentadecene
* 33.083 min.
Counts
Acquisition Time (min)
+ Deconvoluted Scan (33.084 min) 4S-Dot-2025-07-12.D
Lib Match Score=89.5
55.1
83.1
150.0
184.1
210.0
29.0
43.0
83.0
Mass-to-Charge (m/z)

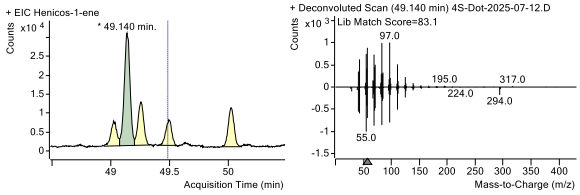

+ EIC 1-Hexadecene
* 36.103 min.
Counts
Acquisition Time (min)
+ Deconvoluted Scan (36.105 min) 4S-Dot-2025-07-12.D
Lib Match Score=94.2
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83.1
196.1
224.0
29.0
69.0
97.0
43.0
Mass-to-Charge (m/z)

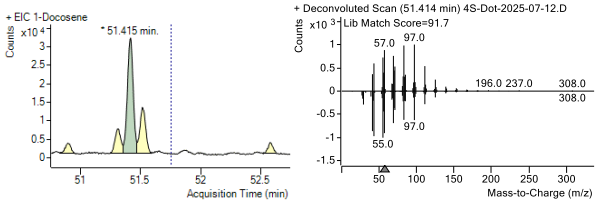

+ EIC 1-Heptadecene
* 38.970 min.
Counts
Acquisition Time (min)
+ Deconvoluted Scan (38.967 min) 4S-Dot-2025-07-12.D
Lib Match Score=86.6
57.1
83.1
152.1
199.0
238.0
57.0
83.0
Mass-to-Charge (m/z)

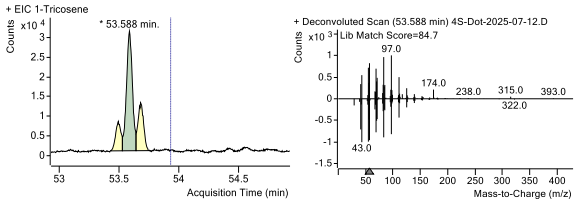

+ EIC 1-Octadecene
* 41.697 min.
Counts
Acquisition Time (min)
+ Deconvoluted Scan (41.695 min) 4S-Dot-2025-07-12.D
Lib Match Score=90.7
83.1
182.1
224.0
252.0
97.0
57.0
Mass-to-Charge (m/z)

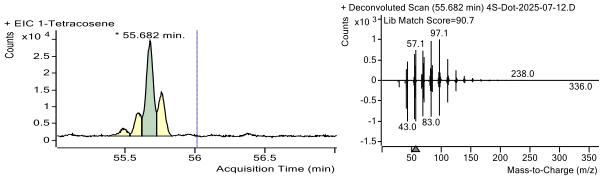

+ EIC 1-Nonadecene
* 44.294 min.
Counts
Acquisition Time (min)
+ Deconvoluted Scan (44.293 min) 4S-Dot-2025-07-12.D
Lib Match Score=91.5
83.0
227.0
266.0
266.0
43.0
97.0
Mass-to-Charge (m/z)


+ EIC 1-Eicosene
* 46.772 min.
Counts
Acquisition Time (min)
+ Deconvoluted Scan (46.771 min) 4S-Dot-2025-07-12.D
Lib Match Score=81.9
57.1
97.1
222.1
280.0
97.0
43.0
Mass-to-Charge (m/z)


+ EIC Henicos-1-ene
* 49.140 min.
Counts
Acquisition Time (min)
+ Deconvoluted Scan (49.140 min) 4S-Dot-2025-07-12.D
Lib Match Score=83.1
97.0
195.0
224.0
317.0
294.0
55.0
Mass-to-Charge (m/z)


+ EIC 1-Docosene
* 51.415 min.
Counts
Acquisition Time (min)
+ Deconvoluted Scan (51.414 min) 4S-Dot-2025-07-12.D
Lib Match Score=91.7
57.0
97.0
196.0
237.0
308.0
308.0
97.0
55.0
Mass-to-Charge (m/z)


+ EIC 1-Tricosene
* 53.588 min.
Counts
Acquisition Time (min)
+ Deconvoluted Scan (53.588 min) 4S-Dot-2025-07-12.D
Lib Match Score=84.7
97.0
174.0
238.0
315.0
393.0
322.0
43.0
Mass-to-Charge (m/z)


+ EIC 1-Tetracosene
* 55.682 min.
Counts
Acquisition Time (min)
+ Deconvoluted Scan (55.682 min) 4S-Dot-2025-07-12.D
Lib Match Score=90.7
57.1
97.1
238.0
336.0
43.0
83.0
Mass-to-Charge (m/z)

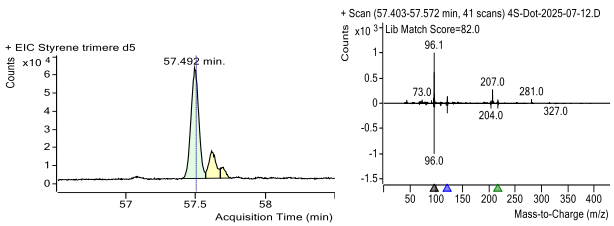


Figure S1. The chromatograms (on the left side) and mass spectrograms (on the right side) through pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) analysis of spiked AH sample, including poly methyl methacrylate cluster (C-PMMA) with 0.075 μg, polyamide-6 cluster (C-PA-6) with 0.135 μg, polypropylene cluster (C-PP) at 1.06 μg, polyvinyl chloride cluster (C-PVC) with 0.88 μg, polyamide-66 (PA-66) with 0.213 μg, styrene-butadiene rubber (SBR) with 0.400 μg, polyethylene terephthalate cluster (C-PET) with 0.251 μg, polycarbonate cluster (C-PC) with 0.08 μg, poly(4-fluorostyrene) ISTD 4PFS at 0.2 μg, Polystyrene cluster (C-PS) with 0.163 μg, polyethylene cluster (C-PE) at 3.29 μg (average sum of α-Alkenes (e.g. C_{14}-C_{22})), and deuterated polystyrene (d5-PS) at 0.2 μg used in internal standard calibration with thermochemolysis (10 % TMAH in MeOH)

4. Measurement standards used in Py-GC/MS

- Polymer-Specific Mass Equivalents of MCS for Calibration Range in Py-GC/MS Analysis

Table S5. Polymer-Specific Mass Equivalents of MCS for Calibration Range in Py-GC/MS Analysis (MSC in SiO_2, low level, Lot: 23031601) example

			Calibration range, low level example						
Polymer	**Abbreviation**	**MCS mg**	**0.11**	**0.22**	**0.30**	**0.49**	**0.62**	**0.94**	**1.18**
Polyethylene	**PE**		0.51	1.02	1.39	2.27	2.87	4.35	5.46
Polypropylene	**PP**		0.13	0.27	0.36	0.59	0.75	1.13	1.42
Polystyrene	**PS**		0.02	0.04	0.06	0.09	0.11	0.17	0.22
Acrylonitrile butadiene styrene	**ABS**		0.03	0.07	0.09	0.15	0.19	0.29	0.37
Styrene butadiene rubber	**SBR**		0.04	0.08	0.11	0.18	0.23	0.35	0.45
Polymethyl methacrylate	**PMMA**	**µg**	0.01	0.02	0.03	0.04	0.05	0.08	0.10
Polycarbonate	**PC**		0.00	0.01	0.01	0.02	0.03	0.04	0.05
Polyvinyl chloride	**PVC**		0.06	0.12	0.17	0.28	0.35	0.53	0.66
Polyethylene terephtalate	**PET**		0.03	0.06	0.09	0.14	0.18	0.27	0.34
Nylon-6	**PA-6**		0.01	0.03	0.04	0.06	0.08	0.12	0.15
Nylon-6,6	**PA-66**		0.03	0.05	0.07	0.12	0.15	0.23	0.29

5. Recovery of microplastic polymer mass fractions (MPs) in spiked samples of AH/VH by Py-GC/MS

Table S6a. Recovery of microplastic polymer mass fractions spiked AH sample (AH 6)

Sample: AH[1] 6				
Polymer cluster	M1[2] µg	M2[3] µg	MS[4] µg	Recovery %
C-PMMA	0.08	0.11	0.05	72.52
C-PA66	0.05	0.21	0.15	105.81
C-PP	N.D.	0.75	0.74	102.42
C-PVC	0.14	0.48	0.34	98.98
C-PA6	0.13	0.21	0.08	109.13
C-PET	0.04	0.18	0.17	79.21
C-PC	N.D.	0.03	0.03	109.09
C-PS	ND.	0.12	0.11	102.39
C-PE	N.D.	4.09	4.21	97.21
C-ABS	N.D.	0.18	0.19	92.54
C-SBR	N.D.	0.20	0.23	86.84

AH[1] aqueous humor sample; M1[2], amount of MPs polymer in sample; M2[3], amount of MPs polymer in spiked sample; MS[4], amount of added polymer (microplastic calibration standard MSC in SiO2, low level, Lot: 23031601, Frontier Lab), poly methyl methacrylate (PMMA), Nylon-6 (PA6), polypropylene (PP), polyvinyl chloride (PVC), Nylon-6.6 (PA66), styrene-butadiene rubber (SBR), polyethylene terephthalate (PET), polycarbonate (PC), poly(4-fluorostyrene) , Polystyrene (PS), polyethylene (PE)

Table S6b. Recovery of microplastic polymer mass fractions spiked VH sample (VH 3)

VH 3[1]				
Polymer cluster	**M1[2]** µg	**M2[3]** µg	**MS[4]** µg	**Recovery %**
C-PMMA	0.068	0.141	0.077	94.55
C-PA66	N.D.	0.181	0.221	81.86
C-PP	N.D.	0.811	1.097	73.90
C-PVC	N.D.	0.417	0.512	81.39

VH 3[1]				
Polymer cluster	M1[2] µg	M2[3] µg	MS[4] µg	Recovery %
C-PA6	N.D.	0.131	0.116	112.67
C-PET	N.D.	0.211	0.259	81.62
C-PC	N.D.	0.048	0.041	116.59
C-PS	N.D.	0.141	0.168	83.75
C-ABS	N.D.	0.185	0.223	82.89
C-SBR	N.D.	0.189	0.272	69.54
C-PE	N.D.	3.304	3.33	99.23

VH[1] vitreous humor sample; M1[2], amount of MPs polymer in sample; M2[3], amount of MPs polymer in spiked sample; MS[4], amount of added polymer (microplastic calibration standard MSC in SiO2, low level, Lot: 23031601, Frontier Lab); poly methyl methacrylate (PMMA), Nylon-6 (N-6, PA6), polypropylene (PP), polyvinyl chloride (PVC),Nylon-6.6 (N-66, PA66) , styrene-butadiene rubber (SBR) polyethylene terephthalate (PET), polycarbonate (PC), poly(4-fluorostyrene) , Polystyrene (PS),polyethylene (PE)

6. Results of Py-GC/MS method development and method performance characteristics in ocular fluids

Table S7. Selected Py-GC/MS method performance indicators in animal ocular internal fluids (aqueous and vitreous humour, AH, VH): linearity range, limit of detection (LOD), limit of quantification (LOQ), recovery and precision (RSDr) for ocular tissues

Indicator compound	Spike Range µg	Linearity range (µg)	LOD µg	LOQ µg	Recovery %		RSD %	
					VH	AH	VH	AH
Methyl methacrylate	PMMA: 0.037-0.055-0.075	0.01-0.10	0.01	0.025	82.42	95.49	9.62	8.24
Cyclopentanone	PA66: 0.104-0.158-0.213	0.03-0.29	0.04	0.062	95.03	95.03	3.85	5.81
2,4-Dimethyl-1-heptene	PP: 0.65-0.88-1.06	0.13 – 1.42	0.079	0.142	74.10	116.52	12.14	5.69
Naphthalene	PVC: 0.43-0.65-0.88	0.06 – 0.98	0.056	0.065	97.70	91.70	3.80	6.02
N-Methyl-ε-caprolactam	PA6: 0.055-0.112-0.135	0.02-0.15	0.02	0.05	89.53	116.52	9.08	5.69
Styrene-butadiene rubber	SBR: 0.245-0.332-0.400	0.04-0.45	0.056	0.10	82.62	92.62	3.50	7.32
Dimethyl terephthalate	PET: 0.126-0.185-0.251	0.03-0.34	0.017	0.034	92.26	91.32	8.72	26.61
p-Methoxy-tert-butylbenzene	PC: 0.030-0.040-0.08	0.006-0.05	0.001	0.006	78.81	81.56	7.29	15.12
2-phenethyl-4-phenylpent-4-enenitrile	ABS: 0.133-0.273-0.329	0.03-0.37	0.015	0.036	107.94	79.95	8.91	0.32
5-Hexene-1,3,5-triyltribenzene	PS: 0.080-0.120-0.163	0.02 -0.22	0.008	0.021	97.05	70.69	7.33	2.80
a series of n-alkene, (average of the areas C14-C24)	PE: 1.99-3.03-3.28	0.51 – 5.46	0.752	2.66	85.4	93.57	6.52	9.76

7. Measurement standards used in UPLC-MS/MS

Bisphenols standards: Analytical standards of BPA (99.0 % purity), BPAF (99.5 %), BPB (98.7 % purity), BPF (96.0 % purity) and BPS (99.6 % purity) were purchased fromSigma-Aldrich (St. Louis, USA). Formic acid was purchased from Sigma-Aldrich (St. Louis, USA). Internal standard 13C-labeled BPS (ring-13C12) was supplied by Cambridge Isotope Laboratories Inc. Acetonitrile (ACN) and methanol (MeOH), used during the sample and standard preparation procedure and as a mobile phase components, were LC-MS grade, obtained from Merck KgaA (Darmstadt, Germany). Dansylchloride 95% - Dns-Cl (Sigma Aldrich, St. Louis, MO, USA) was used as derivatization reagent. Ultrapure water was produced by a Millipore Direct-Q 3 UV system (Millipore, Molsheim, France). Individual stock solutions (1 mg/mL) of all analytes were prepared by dissolving accurately weighted amounts of analytical standards in MeOH. Working solution was obtained by mixing the stock solutions and diluting the mixture with ACN. All solutions were stored in a freezer (−20 °C). All glassware was pre-washed with methanol. Five-point (0.75, 1.5, 5, 10 and 20 ng/mL) matrix-matched calibration curves were prepared using normal human blood serum. Before use, the serum used for preparation of the calibration curves, was analyzed for the presence of analytes under the study. Internal standard (IS) concentration was kept at 10 ng/mL in all calibration samples.

8. Results of UPLC-MS/MS method development – optimised parameters for derivatized bisphenols and method performance characteristics in blood serum

Table S8. Optimised parameters for the mass spectrometry analysis of derivatized bisphenols

Analyte	Precursor ion	Product ion	Collision energy (mV)	Fragmentor V	Dwell time (ms)
BPA	695.4	461.3	36	180	50
BPA		170.1	56	180	50
BPAF	803.4	234.9	42	150	50
BPAF		171.1	56	150	50
BPB	709.4	234.9	38	170	50
BPB		171.1	56	170	50
BPF	667.4	234.9	34	160	50
BPF		169.8	50	160	50
BPS	717.3	234.8	36	160	50
BPS		171.1	50	160	50
24 BPS 13 C 12	729.5	495.2	35	160	50

Bisphenol A (BPA), bisphenol AF (BPAF), bisphenol B (BPB), bisphenol F (BPF) and bisphenol S (BPS)

Table S9. Method performance criteria of UPLC-MS/MS method developed in human blood serum

Bisphenols	Linearity (R^2)	LOD ng/ml	LOQ ng/ml	Recovery %	RSD %
Bisphenol A (BPA) 4-[2-(4-hydroxyphenyl) propan-2-yl]phenol	0.99	0.25	1.0	85.16	17.03
Bisphenol B (BPB)	0.99	0.25	1.0	100.00	8.51

Bisphenols	Linearity (R^2)	LOD ng/ml	LOQ ng/ml	Recovery %	RSD %
4-[2-(4-hydroxyphenyl) butan-2-yl]phenol					
Bisphenol F (BPF) 4-[(4-hydroxyphenyl) methyl]phenol	0.99	0.10	2.0	91.68	9.51
Bisphenol S (BPS) 4-(4-hydroxyphenyl) sulfonylphenol	0.99	1.0	5.0	100.00	15.61
Bisphenol AF (BPAF) 4-[1,1,1,3,3,3-hexafluoro-2-(4-hydroxyphenyl) propan-2-yl]phenol	0.99	0.25	1.0	93.27	19.27